STUDY OF OXIDIZED FLAVOR IN MILK

BY

WILLARD JASON CORBETT

B.S., University of Illinois, 1934

M.S., University of Wisconsin, 1935

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
DAIRY HUSBANDRY IN THE GRADUATE SCHOOL
OF THE UNIVERSITY OF ILLINOIS, 1942

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STUDY OF OXIDIZED FLAVOR IN MILK

Each day approximately fifty million quarts of milk are consumed in fluid form by people in the United States. Nutritionists claim that this is only about half as much milk as should be included in an adequate diet. Further it is recommended by nutritionists that approximately one-fourth of the diet consist of dairy products. For milk to maintain such an important position in the human diet it is imperative that it measure up to certain quality standards. The most important requirements are:

1. Milk must be safe, should be non-toxic and free from disease producing organisms.

2. Have good keeping quality. Since milk is purchased once a day or less frequently it is essential that milk remain free of bacterial fermentation and maintain its original flavor for several days.

3. For aesthetical reasons it is essential that milk be handled under conditions conducive to cleanliness both on the farm and in the processing plant.

4. That milk have a high food value—most states and municipalities have statuatory laws defining the minimum fat and milk solids-not-fat content of milk.

5. That milk have a palatable flavor.

6. That milk be of uniform quality.

The advancement in knowledge in milk technology, the nearly universal use of pasteurization, improvement in design and type of equipment, availability of trained personnel, and supervision of milk supplies by both the industry and regulatory officials have been of immense value in improving milk in the above respects.

It is quite probable that milk is so extensively used as a beverage largely because of its palatable flavor. A good example of this is the rapid consumer acceptance of homogenized milk, a product of superior drinking qualities due to its richer flavor. If milk is to maintain its dominant position in the diet

it will have to compete with other food products primarily on a palatability basis since many of the excellent food nutrients contained in milk can be supplied from other sources.

Milk is very sensitive to physical and biological factors which may bring about changes in the flavor. Common factors affecting milk flavor are individuality of the cow, stage of lactation, infection of the udder, feed, bacterial fermentation, contamination by volatile foreign substances, enzymatic or chemical changes, heat treatment, contamination by certain metals, and exposure to light.

One of the most common and most objectionable defects in market milk is the oxidized flavor. Golding and Feilmann[1] (1905) were the first investigators to report on the oxidized flavor of milk. They traced the defect to a copper exposed cooler which was being used by a dairy experiencing the flavor difficulty. By replacing the old cooler with a new well-tinned cooler no further difficulty was experienced. They described the defect as an "alkaline mealy flavor". They pointed out that the defect was less likely to occur in summer than in winter, and that the off-flavor was less marked in milk with a high bacterial count. In 1920 Hammer and Cordes[2] noted that milk exposed to light developed a "tallowy" like flavor. Frazier[3] later confirmed this. He observed that milk exposed to diffused light for 8 hours developed a "cardboard" or "linseed oil" like flavor. Tracy and Ruehe[4] in 1931 also observed this effect from light but noted that in addition to the "tallowiness" a "burnt" like flavor was sometimes present. This "burnt" flavor was thought to be due to a protein reaction rather than a fat oxidation. Tracy and Ruehe also showed the pro-oxidant effect of dissolved metals on the development of the off-flavor. Since these early investigations many papers have been published relative to the oxidized flavor in dairy products. Brown and Thurston[5] in a complete review of the subject in the Journal of Dairy Science, July, 1940, included a bibliography containing over four hundred references. The tremendous amount of research work which has been done on the problem is evidence of the seriousness of the defect.

This off-flavor has been described in various ways, possibly because of the different degrees of development that may occur causing different flavor reactions. Such terms as oily, cappy, papery, astringent, tallowy, and metallic have been used. Not only is the oxidized flavor in dairy products modified by the intermediate and end products formed during oxidation, but it is also influenced by the presence of certain metallic salts which in some cases may be detected by taste before the true oxidized flavor becomes evident.

The defect did not become prevalent until after the first World War. There are numerous circumstances coincident with the occurrence of the oxidized flavor. The defect is not evident in milk at the time it is secreted, but develops usually within 24 to 72 hours afterwards. The off-flavor is catalyzed by the addition of certain metallic salts, copper being the most effective. Equipment surfaces made of the copper-nickel alloys as Ambrac A have been common causes of oxidized flavor in dairy products. Presence of large numbers of bacteria retard or prevent the off-flavor from developing, hence the flavor is less likely to occur in low quality milk. Pasteurization of milk tends to increase the incidence of the defect, especially if the hot milk is brought in contact with copper bearing metals. The off-flavor occurs more frenquently in winter than summer months. This is probably due to the type of feed (less green feed) the cow receives during the winter months and because winter milk generally has a lower bacterial count than summer milk. The universal use of electric refrigerators with the longer holding of milk has undoubtedly been an important factor in the greater incidence of oxidized flavor.

The relation between bacterial content and the development of oxidized flavors has led certain individuals to question the wisdom of producing milk with low count. A milk with a strong oxidized flavor will be objected to by most discriminating customers. It is apparent, therefore, that if the industry continues to improve the sanitary quality of mar-

ket milk supplies it is essential that effective methods for controlling oxidized flavor be developed.

PLAN OF STUDY

This investigation was undertaken to secure more information regarding the occurrence, factors effecting, and methods for controlling this off-flavor. The study is reported in five parts.

Part 1. Extent of oxidized flavor in the milk from individual cows in the University herd was investigated. The relation between occurrence of oxidized flavor and breed and age of the cow, period of lactation, season of the year, milk yield, fat yield and composition of the milk was determined.

Part 2. This phase of the thesis was initiated to obtain more information regarding the substance in milk concerned with the oxidized flavor. The mechanism by which certain processes retard or prevent the development of the off-flavor was also investigated.

Part 3. Since it is known that both feed and atmospheric conditions are likely to alter the degree of saturation of the milk fat, and also that feed and atmospheric conditions affect the occurrence of oxidized flavor, it was deemed desirable to determine the relation, if any, between the saturation of the milk fat and occurrence of oxidized flavors.

Part 4. Since oxygen is essential in any oxidation reaction it was thought desirable to determine the relation of the gas content of milk to development of the oxidized flavor. The gas content of the milk was varied by bubbling various gases through milk, by subjecting milk to various gases under pressure, and by subjecting milk to a vacuum treatment. The application of the polarigraphic method for determining the oxygen content of milk was investigated.

Part 5. This phase was concerned by investigating the possibilities of using anti-oxidants for preventing or controlling the oxidized flavor.

RESULTS OF THE STUDY

Part 1. The development of oxidized flavor in the milk from individual cows in the University herd was studied at monthly intervals from March through July and again in September. To determine the susceptibility of each cow's milk to oxidized flavor each sample was divided into two lots and to one portion copper (1 p.p.m.) was added. Altogether 538 samples were studied. Of the metal-free milks 1.48 percent developed an oxidized flavor in 24 hours and 10.01 percent in 3 day's storage at 40°F. Of the copper contaminated samples 78.5 percent were oxidized at the end of 24 hours and 91.7 percent at the end of 72 hours. Within the period in which the observations were made there was no correlation between the occurrence of oxidized flavor and the season. However, the intensity of the oxidized flavor was greater during the winter months.

Of the five breeds of cows from which samples were taken the milk from the Ayrshire breed seemed least susceptible to spontaneous and metal-induced oxidized flavor. The milk from the other four breeds (Brown Swiss, Jersey, Guernsey, and Holstein) varied little in its tendency to become oxidized.

The stage of lactation was correlated with development of oxidized flavor. Milk (metal-free) produced from cows in the first month or two of lactation was more susceptible to oxidation than that from cows in the later part of their lactation. The extend of oxidized flavor in the copper contaminated samples appeared independent of stage of lactation. Milk from younger cows was more susceptible to oxidation than that produced by older animals. Milk from heifers in the first month or two of lactation was especially susceptible to development of the flavor defect.

Development of oxidized flavor was not correlated with weekly milk or fat yield.

The milk from three groups of cows whose milk varied in its susceptibility to development of oxidized flavor was examined for fat, solids-not-fat, oxygen and ascorbic acid con-

tent, creaming ability, titratable acidity, pH, curd tension and fat globule size. Although wide variations occurred in the results obtained on the different samples none of the values could be correlated with the extent of oxidized flavor development.

Part 2. The relation between the fat globule membrane and development of oxidized flavor was investigated. Attempts were made to follow the development of oxidized flavor by measuring the iodine number of phospholipins from normal and oxidized milk. A procedure developed by Swanson and Sommer[6] was used for purifying the phospholipids. Inconsistent results were obtained in these experiments suggesting that either the procedure was at fault or that development of oxidized flavor is not related to oxidation of phospholipins as measured by changes in the iodine number. Milk made from "washed" cream (fat globule removed by repeated washing with water) and skimmilk developed a typical oxidized flavor. Increasing the phospholipid content of milk by combining cream and buttermilk (high in phospholipid) did not increase the susceptibility of fat to oxidation. Since it was impossible to follow the development of oxidized flavor by changes in the oxidation of the fat globule membrane material and since milk mixtures practically free of phospholipids developed an oxidized flavor it is evident that the oxidized flavor can be caused by oxidation of the butterfat and is not limited to oxidation of the fat globule membrance as some contend.

The effect of homogenization and agitation in retarding oxidized flavor can best be explained on the basis that during these processes a protective membrane is formed around the fat globule. This membrane is thought to be adsorbed on the fat globule in such a manner to protect the fat from the catalysts contained in the serum.

Heating milk at high temperatures retards oxidized flavor in the case of metal-free milk and milk contaminated with copper previous to the heat treatment. On the other hand

milk contaminated with copper after the heat treatment is susceptible to development of oxidized flavor. The effect of heating metal-free milk on oxidation-reduction potentials suggests that reducing substances are formed during the heat treatment. The fact that the addition of copper to milk prior to heating retards the development of oxidized flavor and that addition of copper after heating catalyzes the off-flavor indicates that in the former case copper is combined with the reducing substance formed and is inactivated. However, the catalytic effect of copper is not neutralized when the contamination takes place after the heat treatment. The origin of the reducing substances appears to be associated with the fat, as heating cream produces more reducing substances than heating the plasma portion. It is possible that the fat globule membrane is the source from which the reducing substances are liberated during the high heat treatment.

Part 3. The relation of the composition of the butterfat to development of oxidized flavor in milk was investigated. Since the degree of saturation of the butterfat was the more likely factor which would be related to the oxidation of the fat, the problem was studied from this angle. The degree of saturation of the milk was varied by inclusion of corn and cocoanut oil in the ration of six animals varying in the susceptibility of their milk to oxidation. The degree of saturation of the milk fat was measured by means of the iodine number and refractive index. Although the degree of saturation of the milk fat was appreciably changed by feeding the oils the susceptibility of the milk to oxidized flavor varied only slightly. There was a slight tendency for milk having a fat iodine number greater than 40 to develop a more intense oxidized flavor than milk having fat with an iodine number lower than 40.

Part 4. Because of the importance of oxygen in any oxidation reaction such as in the development of oxidized flavor it seemed desirable to develop a more rapid and simple method than those now aviliable for measuring the oxygen concentration in milk. The adoptation of the polarigraphic method in-

volving the use of a dropping mercury electrode was found to give satisfactory results for this determination. Mixed milk and milk from individual cows was found to contain from 5 to 7 mgs. per liter of oxygen. Such factors as bacterial growth, heat treatment and contamination by certain metals was found to effect the amount of oxygen in the milk.

Storing milk under pressure of carbon dioxide and nitrous oxide prevented the development of oxidized flavor as well as the oxidation of ascorbic acid. Storing milk under pressure of oxygen gas retarded the development of oxidized flavor, but accelerated the oxidation of ascorbic acid. Milk stored under pressure of nitrogen developed an oxidized flavor more readily than that stored under atmospheric pressure.

Condensing milk under partial vacuum retarded the development of oxidized flavor in the condensed milk as well as the condensed milk reconstituted with water to the original solids concentration. The amount of retardation varied directly with the extent of which the milk was condensed. The retardation did not appear related to the oxygen concentration of the milk. Milk made from condensed skimmilk, cream and water was very resistant to development of oxidized flavor, although milk made from the same lots of cream and skimmilk developed an oxidized flavor very readily. These facts suggest that during the condensing process some antioxidant substances are liberated which are able to retard oxidation of the fat.

Part 5. Tyrosine and the more soluble esters of tyrosine were found to be effective antioxidants when used in milk in concentrations of .02 to .04 percent. Hydroquinone, a substance having similar chemical properties, was an effective antitoxidant when added at the rate of 5 to 10 p.p.m. The normal amyl ester of leucine was also an effective antioxidant, but imparted an objectionable off-flavor to the milk.

The addition of 10 to 100 milligrams of ascorbic acid per liter of milk gave variable results. In metal-free milk, the addition of ascorbic acid retarded but did not prevent the development of oxidized flavor. In copper contaminated milk

the ascorbic acid first retarded the development of an oxidized flavor and then after a certain point was reached, the oxidation was accelerated.

The addition of pancreatic extract in the proportion of one part extract to 25,000 parts milk effectively prevented the development of the flavor defect.

The addition of cereal grains or the concentrated water extracts of the cereal grains was found to delay the development of an oxidized flavor in milk. An effective antioxidant was prepared by drying a mixture of a water extract of a cereal flour and concentrated skimmilk.

Homogenizing milk or adding N butyl ester of tyrosine, pancreatic extract, or cereal flours had no effect on the oxidation of ascorbic acid though they did retard or entirely prevent the development of oxidized flavor. This indicates that oxidation of ascorbic acid is not as intimately connected with the development of oxidized flavor as some suggest.

CONCLUSIONS

From the results of this investigation the following conclusions are drawn:

1. Milks from individual cows vary in their susceptibility to the development of oxidized flavor. This variation was correlated to stage of lactation and age of animal, but was only slightly correlated to season of the year (within the period March through September) and breed. The amount of milk and fat produced weekly was not related to the development of the off-flavor.

2. Oxidized flavor can be developed in milk in which the fat globule membrane has been removed, proving that oxidized flavor can result from an oxidation of the butterfat.

3. Homogenization retards the development of oxidized flavor by enveloping the fat globule in a protective casein membrane.

4. High heat treatment retards oxidized flavor development through the production of reducing substances, which compounds likely exert an antioxidant effect.

5. The degree of saturation of the milk fat is only slightly correlated to development of oxidized flavor in the milk.

6. A dropping mercury electrode method was found suitable for measuring the oxygen content of milk.

7. The development of oxidized flavor can be prevented by storing milk under several atmospheres of carbon dioxide or nitrous oxide and retarded by storing under pressure of oxygen.

8. Storing milk under atmospheres of nitrogen hastened the development of oxidized flavor.

9. Condensing milk under vacuum to a concentration of approximately 2 to 1 prevented the development of oxidized flavor in both the condensed milk and condensed milk reconstituted to the original solids concentration.

10. Four percent fat milk made from condensed skimmilk and 32 percent cream did not develop an oxidized flavor, even when copper was added at the rate of 3 p.p.m.

11. The effect of condensing in retarding oxidized flavor development is thought to be due to the liberation in the milk of certain antioxidative constituents, derivatives of the plasma solids.

12. The addition of certain antioxidants to milk retarded or entirely prevented the development of oxidized flavor. The most effective antioxidants were hydroquinone, tyrosine or soluble esters of tyrosine and a pancreatic extract. Other less effective antioxidants were ascorbic acid, extract of the cereal grains and certain amino acids.

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VITA

I was born near Pearl City, Illinois, on October 29, 1912. I lived in Adams County, North Dakota, until 12 years of age where I attended the first six grades. I graduated from elementary grade school in Stephenson County, Illinois, in 1926 and from Shannon High School in 1930. I entered the University of Illinois College of Agriculture in September, 1930, and received a B.S. degree in 1934. I was recipient of a Dairy and Ice Cream Machinery and Supplies Judging fellowship at the University of Wisconsin for the year 1934-35 during which time I completed work for the degree of M.S. In 1935 I was appointed full-time assistant in Dairy Husbandry in which position I was employed until January 1, 1942, when I accepted a position with the Telling Belle Vernon Company, Cleveland, Ohio. In 1936 I was married to Alice Carman.

I have been elected to the following honorary societies: Gamma Sigma Delta, 1937; Associate Sigma Xi, 1937; and member of Sigma Xi, 1940.

I have published a total of 24 articles pertaining to my research work in Dairy Manufactures.